PB81-233819

Origins of Polycyclic Aromatic Hydrocarbons in Estuarine Sediments

Rhode Island Univ.
Narragansett

Prepared for

Environmental Research Lab.
Narragansett, RI

20 Jul 79

U.S. Department of Commerce
National Technical Information Service
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TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3. RECIP
EPA-600/J-79-134	Journal Article	PB81-233819

4. TITLE AND SUBTITLE	5. REPORT DATE
Origins of polycyclic aromatic hydrocarbons in estuarine sediments	July 1981
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J. Lake, C. Norwood, C. Dimock, and R. Bowen	ERLN-X9
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Protection Agency- Research Laboratory South Ferry Road, Narragansett, RI 02882 URI Graduate School of Oceanography Narragansett, RI 02882	ACULIA
	11. CONTRACT/GRANT NO.
	R 802724
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Research Laboratory South Ferry Road Narragansett, Rhode Island 02882	Journal Article
	14. SPONSORING AGENCY CODE
	EPA/600/05

15. SUPPLEMENTARY NOTES

This project has been financed in part by funds from the Environmental Protection Agency

16. ABSTRACT

Abstract—In order to determine the origin of polycyclic aromatic hydrocarbons (PAHs) in sediments from Narragansett Bay, Rhode Island, the PAH assemblages from the sediments and from possible origin materials were analyzed by gas chromatographic and gas chromatographic-mass spectrometric techniques. Analyses included determinations of: (1) the relative content of non-alkylated PAH parent molecules, i.e. parent compound distributions (PCDs); (2) alkylation patterns of these PAH molecules, i.e. alkyl homolog distributions (AHDs); and (3) phenanthrene/anthracene (P/A) ratios. Samples from the Narragansett Bay transect, which began at a sewage outfall for the City of East Providence, Rhode Island, and ended 20 km to the south, showed rapidly decreasing concentrations of PAH compounds with increasing distance from Providence. The PAH assemblages in transect sediment samples, and in other samples collected near piers, showed evidence for different origins. The sediments surrounding tarred piers were contaminated by coal tar used to coat the pilings. The close resemblance of PCDs from bay sediments and combustion products indicated that the PAHs in the transect sediments were predominantly combustion generated. While evidence for the input of PAHs from petroleum to bay sediments appeared in some AHDs of upper bay transect sediments, AHDs from the lower (less polluted) end of the transect showed less influence of petroleum PAH contamination. In general, the shapes of AHDs from transect sediments of Narragansett Bay appeared to be best explained by a combination of inputs of PAHs from petroleum and combustion processes, rather than by the solubility alteration of PAH assemblages on incoming airborne material.

Geochimica et Cosmochimica
Acta 43, 1847-1854 (1979)

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
unlimited	unclassified	
	20. SECURITY CLASS *(This page)*	22. PRICE
	unclassified	

EPA Form 2220-1 (9-73)

Geochimica et Cosmochimica Acta Vol. 43, pp. 1847 to 1854
Pergamon Press Ltd. 1979. Printed in Great Britain

0016-7037/79/1101-1847$02.00/0

EPA-600/J-79-134
Journal Article

Origins of polycyclic aromatic hydrocarbons in estuarine sediments

JAMES L. LAKE[1], CURTIS NORWOOD[1], CRANDALL DIMOCK[2] and ROBERT BOWEN[2]

[1]Environmental Protection Agency, Narragansett, Rhode Island, U.S.A.
[2]University of Rhode Island Graduate School of Oceanography, Narragansett, Rhode Island, U.S.A.

(*Received* 1 *March* 1979; *accepted in revised form* 20 *July* 1979)

Abstract—In order to determine the origin of polycyclic aromatic hydrocarbons (PAHs) in sediments from Narragansett Bay, Rhode Island, the PAH assemblages from the sediments and from possible origin materials were analyzed by gas chromatographic and gas chromatographic–mass spectrometric techniques. Analyses included determinations of: (1) the relative content of non-alkylated PAH parent molecules, i.e. parent compound distributions (PCDs); (2) alkylation patterns of these PAH molecules, i.e. alkyl homolog distributions (AHDs); and (3) phenanthrene/anthracene (P/A) ratios. Samples from the Narragansett Bay transect, which began at a sewage outfall for the City of East Providence, Rhode Island, and ended 20 km to the south, showed rapidly decreasing concentrations of PAH compounds with increasing distance from Providence. The PAH assemblages in transect sediment samples, and in other samples collected near piers, showed evidence for different origins. The sediments surrounding tarred piers were contaminated by coal tar used to coat the pilings. The close resemblance of PCDs from bay sediments and combustion products indicated that the PAHs in the transect sediments were predominantly combustion generated. While evidence for the input of PAHs from petroleum to bay sediments appeared in some AHDs of upper bay transect sediments, AHDs from the lower (less polluted) end of the transect showed less influence of petroleum PAH contamination. In general, the shapes of AHDs from transect sediments of Narragansett Bay appeared to be best explained by a combination of inputs of PAHs from petroleum and combustion processes, rather than by the solubility alteration of PAH assemblages on incoming airborne material.

INTRODUCTION

INTEREST in determining the polycyclic aromatic hydrocarbon (PAH) content of environmental samples has been generated due to health hazards associated with these compounds and because a knowledge of the sources, fates, and effects of these compounds may aid in assessments of man's impact on his environment. Since marine sediments are repositories for many air and waterborne pollutants, researchers have examined the relative content of parent non-alkylated PAH molecules and the distributions of the alkyl homologs of PAHs in marine sediment samples (WINDSOR and HITES, 1979; HITES, 1976; LAFLAMME and HITES, 1978; YOUNGBLOOD and BLUMER, 1975; HITES *et al.*, 1977, BLUMER and YOUNGBLOOD, 1975; HASE and HITES, 1976; GIGER and BLUMER, 1974; HITES and BIEMANN, 1975; FARRINGTON *et al.*, 1977). Recent work has determined the content of parent PAH molecules in marine sediments (WINDSOR and HITES, 1979). Other research has hypothesized about the origins of the PAH assemblages in marine sediments from comparisons of their alkyl homolog distributions with those found in airborne particulate material (HASE and HITES, 1976), combustion products of fossil fuels (LEE *et al.*, 1977; HASE and HITES, 1976), petroleum (YOUNGBLOOD and BLUMER, 1975) and water (HASE and HITES, 1976).

Other studies have found variations in aqueous solubilities of PAH molecules (MAY *et al.*, 1978). These solubility differences and differences in the reactivities of these compounds in the atmosphere (NATIONAL ACADEMY OF SCIENCE, 1972) and in the water (RADDING *et al.*, 1976) may have resulted in processes which altered PAH assemblages in the environment. These processes or others (i.e. selective bacterial degradation) could have caused the differences observed in PAH assemblages from origin material and from marine sediments (HITES, 1976; HASE and HITES, 1976; LAFLAME and HITES, 1978). Other inputs of PAH's to marine sediments, however, may also have caused these differences.

The present study examined the PAH content, the alkyl homolog distributions (AHDs) and the relative content of non-alkylated PAH compounds or parent compound distributions (PCDs) obtained from sediment samples taken from Narragansett Bay, Rhode Island. Comparisons of these measurements with those from several PAH origin materials were made to determine the dominant origins of the PAH compounds contaminating this New England estuarine environment.

The present study also examined the phenanthrene/anthracene ratio (P/A) as a means of describing the PAH assemblages in environmental samples. Due to differences in reactivity (NATIONAL ACADEMY OF SCIENCE, 1972) and solubility (MAY *et al.*, 1978) of these two isomers, this ratio was not expected to remain constant and thereby provide a tracer of PAH molecules from origin, through environmental transport, to deposition in marine sediments. Rather, it was hoped that comparisons of this ratio for origin

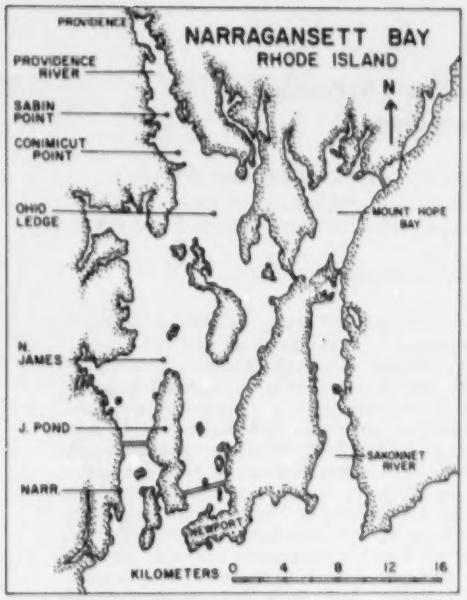

Fig. 1. Map of Narragansett Bay, Rhode Island, showing sampling locations.

material, and marine sediments would provide some insight into environmental modification of PAH assemblages.

METHODS

Sediment samples, taken along a transect in the Narragansett Bay (Fig. 1), were obtained by divers using plexiglas core tubes. The water depth was 7 m at all transect stations. The water at the upper bay stations, Sabin Point and Conimicut Point, near the city of Providence, was brown and thus indicative of high levels of suspended particulates; whereas the water at the lower bay stations was clear. Samples of sediments taken near piers in the Narragansett Bay and in New Harbor on Block Island, Rhode Island, were collected with a Ponar grab sampler. A sediment sample from a shallow (0.5–1 m depth) anaerobic pond on Jamestown Island, Rhode Island, was obtained with a plexiglas core tube.

All sediment samples were returned to the laboratory as quickly as possible and analyzed immediately or frozen at −20°C until analysis. Prior to analysis of the top 10-cm section of the core, the sediment contacting the plexiglas core liner was scraped off.

The extraction and clean up procedures used on sediment samples have been described elsewhere (LAKE *et al.*, 1979). Briefly, this method consists of a methylene chloride reflux extraction followed by separation of the extract into fraction F-1 (aliphatic hydrocarbons, including some olefins) and fraction F-2 (aromatic hydrocarbons, including some olefins) on a silica gel column. In comparison to some other methods, the methylene chloride reflux extraction has been shown to be less efficient for the extraction of F-1 fractions from sediments, but equally efficient for the extraction of F-2 (including PAHs) material (LAKE *et al.*, 1979).

Samples of dock tar were obtained by scraping coal tar from pilings and piers. The soot sample was obtained from the interior of a wood burning stove. Samples of No. 2 fuel oil were obtained from Exxon in Houston, Texas. The motor oil was collected from the crankcase of a 1966 Chevrolet. The oil in this car had not been changed for at least 6 months.

Soot and tar samples were dissolved in CH_2Cl_2 solvent exchanged to hexane and separated into F-1 and F-2 fractions on silica gel columns. The oil samples were dissolved in hexane and fractionated on the silica gel column.

The extracts were analyzed by a combination of gas chromatography (GC) and gas chromatography mass spectrometry (GC–MS). The GC analyses were performed on a 20-m glass capillary column coated with SE-54 in a Hewlett–Packard 5840A GC with splitless injection. The GC–MS analyses were performed on a similar column in a Shimazdu Model GC-4CM GC with splitless injection. This GC was connected to a Finnegan 1015 mass spectrometer equipped with a Systems Industries data system and Riber 400 D-8 software. The mass spectrometer was operated in the electron impact mode at 70 eV.

Concentrations of PAH compounds were determined by GC or GC–MS quantitation techniques. For the transect sediment samples, GC techniques involving external standards and a digitizing planimeter were used to quantitate selected PAH compounds (Fig. 2). The remaining quanti-

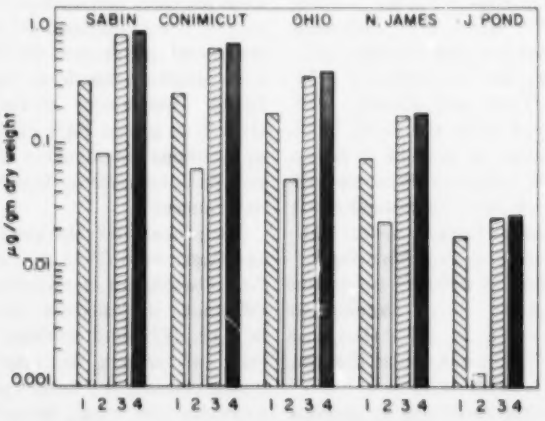

Fig. 2. Concentrations of individual PAHs for the bay transect sediments. 1 = Phenanthrene; 2 = anthracene; 3 = fluoranthene; 4 = pyrene.

tations resulted from GC–MS techniques which consisted of integrating extracted ion current profiles (EICPs) corresponding to the molecular ions of the compounds of interest. Specific peaks in the EICPs were not integrated if their spectra did not correspond to those of the compounds of interest or if they did not have characteristic retention times. The concentrations were normalized and displayed in a semi-logarithmic format as PCDs and AHDs. PCDs represent the relative concentrations of the parent compounds of interest; i.e. PAHs with molecular weights of 178, 202, 228, 252, 276, and 278. These distributions were obtained by correcting the raw data for instrument response with the aid of response factors calculated from known PAH standards. In the few cases where a standard was not available, raw data were corrected by the use of another PAH standard with the same molecular weight. AHDs show the concentration of the parent compound in relation to its C_1 through C_3 alkyl homologs. In general the AHDs were not corrected for instrument response because of a lack of necessary standards. However, to enable rough comparisons with cited literature, the $Z = -18$ and $Z = -22$ AHDs (determined from the formula C_nH_{2n+z}) from the pond sample were corrected using the three alkylated PAH standards that were available. P/As were calculated by integrating separately the areas under the two peaks in the EIC[3] for m/e of 178.

Reagent blanks and standard samples were processed along with the samples to ensure continued satisfactory performance of the methods.

The precision and accuracy of the methods used have been found to be very good and have been previously reported (LAKE *et al.*, 1979).

RESULTS

The concentrations of phenanthrene, anthracene, fluoranthene and pyrene found in the transect sediment samples and in the sediment sample from Jamestown Pond are shown in Fig. 2. While the absolute concentrations of each of these compounds in the transect sediment samples decreased with increased distance from Providence, the relative content of these compounds remained remarkably similar. The PCDs from the transect sediment samples were similar to each other (Fig. 3). The $Z = -18$ AHDs (phenanthrenes and anthracenes) from the Sabin Point sample maximized at the C_1 homolog, but the relative content of this homolog decreased with increased distance from Providence (Fig. 4). The $Z = -22$ AHDs (fluoranthenes and pyrenes) from all transect sediments maximized at the C_0 rather than the C_1 homolog and showed a relative decrease in the abundance of alkylated species at the lower bay stations (Fig. 5). The P/As from the transect sediment samples were relatively low and constant (3.0–4.3) (Table 1).

Table 1. Phenanthrene/anthracene ratios (P/As) for sediment samples and for materials representative of possible origins of PAHs in the marine environment

P/A ratio	Sample type
4.0	Sabin Point sediment
4.3	Conimicut Point sediment
3.0	Ohio Ledge sediment
4.3	North Jamestown sediment
18	Jamestown Pond sediment
50	No. 2 fuel oil
17	Wood stove soot
8	Used crankcase oil
23–38	Dock tar and sediment

Samples of the coal tar used to coat pilings and docks and samples of the sediments surrounding docks from Narragansett Bay and from Block Island, Rhode Island, showed similar PCDs, $Z = -18$ and $Z = -22$ AHDs and P/As. However, as a group, these characteristics were quite different from

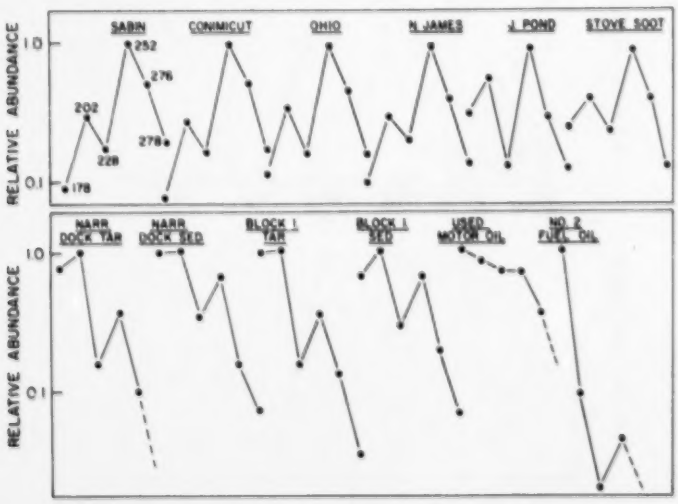

Fig. 3. Parent Compound Distributions (PCDs) for sediment samples and for materials representative of possible origins of PAHs in the marine environment. (Data corrected for instrument response.)

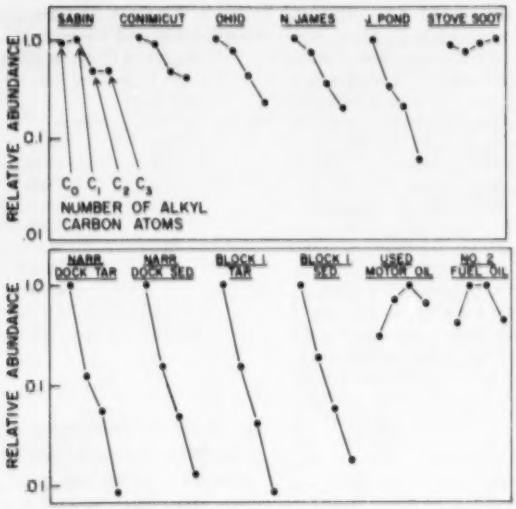

Fig. 4. Z = −18 alkyl-homolog distributions (AHDs) (phenanthrenes and anthracenes) for sediment samples and for materials representative of possible origins of PAHs in the marine environment. (Data not corrected for instrument response.)

those for the transect sediments, as can be readily seen in Figs 3–5 and Table 1.

The PCDs from No. 2 fuel oil and used crankcase oil were distinctly different from each other and from PCDs of either transect sediment or coal tar samples (Fig. 3). In addition, the Z = −18 and Z = −22 AHDs from these two oils were very different from those of either the transect or coal tar samples (Figs 4 and 5). These distributions maximized in the alkylated homolog range, rather than at the parent compound (Figs 4 and 5). The P/A of the No. 2 fuel oil was very high (50) while that from the used crankcase oil was 8.

The PCDs from wood stove combustion products, the pond sediments, and the bay transect sediment samples were quite similar (Fig. 3). The Z = −18 and Z = −22 AHDs from the wood stove showed relatively high abundances of alkylated vs non-alkylated PAH compounds (Figs 4 and 5). In contrast, the pond

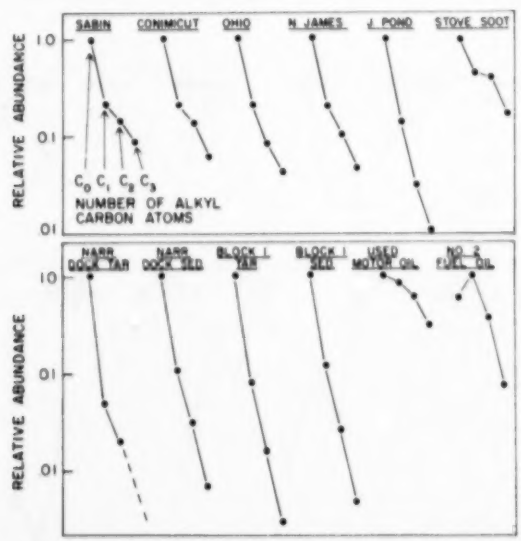

Fig. 5. Z = −22 alkyl-homolog distributions (AHDs) (e.g. fluoranthenes and pyrenes) for sediment samples and for materials representative of possible origins of PAHs in the marine environment. (Data not corrected for instrument response.)

sediment sample showed a low abundance of alkylated vs non-alkylated PAH compounds in the $Z = -18$ and $Z = -22$ AHDs (Figs 4 and 5). The P/As of the stove soot and the pond sediment were 17 and 18, respectively.

DISCUSSION

The data from the transect sediments in the present study showed decreasing concentrations of PAH compounds in sediment samples with increasing distance from the city of Providence (Fig. 2). These data, the similarities of PCDs, $Z = -18$ and $Z = -22$ AHDs, and the P/As (Figs 3–5; Table 1) indicated that the city of Providence was a likely source for much of the PAH content of transect sediments, but the determination of the dominant origin of these compounds was found to be a difficult task. This task was complicated because the nature and magnitude of PAH inputs to this estuarine environment were unknown, and because it was not known whether transformation of PAH assemblages had occurred during transport and/or following deposition of these compounds in marine sediments.

An examination of the PAH assemblages in extracts of sediments obtained near piers in the Narragansett Bay was undertaken to determine if the coal tar used to coat these piers was a significant source of PAHs to Narragansett Bay sediments. Comparisons of PCDs, AHDs, and P/As from the sediments near the docks with those obtained from the coal tar used to coat the docks showed that PAHs from coal tar were present in the surrounding sediments. The PAH assemblages in the dock tar and in these contaminated sediments showed characteristic PCDs (Fig. 3), steeply sloping $Z = -18$ and $Z = -22$ AHDs (Figs 4 and 5), and relatively high ($\geqslant 23$) P/A ratios (Table 1). To ensure that other inputs of PAH material were not influencing the observed measurements, samples of dock tar and sediments were obtained from a relatively pristine location—Block Island, Rhode Island (25 km off the coast of Rhode Island). The PAH measurements from these samples matched each other and those from corresponding tar and sediment samples from Narragansett Bay. While these data show that the use of coal tar in marine construction resulted in the input of PAH compounds to marine sediments adjacent to the docks, comparisons of PCDs, AHDs, and P/As of these sediments with those from the transect sediments (Figs 3–5; Table 1) indicated that dock tar was probably not the major PAH contaminant of the transect sediment samples.

The present study proposes that a combination of inputs of petroleum and combustion products was responsible for the observed distributions of PAHs in the Narragansett Bay transect sediments. Although past research has proposed that used crankcase oil and other petroleum oils entered Narragansett Bay via the sewage systems and appeared as unresolved hydrocarbon material in the extracts of sediments (Van Vleet and Quinn, 1977), the PAH content of the sediments was not determined. In the present study this input is represented by the used motor oil and No. 2 fuel oil samples.

Another input of PAH material to the Narragansett Bay results from the deposition of aeolian transported fossil fuel combustion products. This combustion input may result from the direct deposition of these compounds from the air into bay water, or from the deposition of PAH containing particles onto land, followed by transport to the bay by runoff. While the quantities of atmospheric inputs of PAH material to the Narragansett Bay are unknown, studies have found the PAH content of atmospheric samples to be much greater in the city of Providence than in the rural southern end of Narragansett Bay (Krstulovic *et al.*, 1977). Since no air samples were obtained in the present study an effort was made to find a sediment sample which would represent the atmospheric input of PAHs. For this purpose a sediment sample from an anaerobic sedimentary environment (Jamestown Pond), where the predominant source of PAH was believed to be from atmospheric inputs, was examined. Further characteristics of PAH distributions in combustion products were obtained from the examination of soot samples taken from a wood burning stove.

The present study compared PCDs, AHDs and P/As of the transect sediments with those from the materials representative of the two suggested inputs. These comparisons revealed an overall predominance of combustion generated PAH in transect sediments, but PAH assemblages from petroleum were also found in upper bay sediments.

The bulk of the PAH material in the transect sediments is non-alkylated; as shown by the facts that all of the major peaks in the chromatograms are parent compounds, and that the AHDs, for the most part, show greatly decreased concentrations of alkylated compounds relative to the non-alkylated parent compounds in each series (Figs 4 and 5). Thus the PCDs are representative of the bulk of the PAH material in the transect sediments. PCDs of the two input materials, however, are distinctly different from each other (Fig. 3). Of the two, the combustion generated PCDs very closely resemble those of the transect sediments, while those representing the petroleum inputs are markedly different. From this evidence it appears that PAH material in transect sediments resulted primarily from combustion inputs. However, an examination of the AHDs shows a more complicated scheme of inputs.

AHDs of the fuel and motor oil samples show high concentrations of the alkylated homologs relative to their parent compounds. In addition, phenanthrene and its alkyl homologs ($Z = -18$ homolog series) were more abundant than fluoranthene and pyrene and their alkyl homologs ($Z = -22$ homolog series) in the oil samples. These findings are consistent with

those of YOUNGBLOOD and BLUMER (1975) and PANCIROV and BROWN (1975) who examined the PAH content of several oils.

The AHDs from the Jamestown Pond samples and the wood stove combustion products were not close matches, but these differences probably resulted because the low temperature of combustion in the wood stove did not provide combustion products which were representative of the dominant combustion origins in the Providence–Narragansett Bay area. Research has shown that the distributions of alkyl homologs of PAH molecules from combustion origins vary depending upon the temperature of combustion. At moderate combustion temperatures (as in the wood stove, or from the combustion of coal (LAFLAMME and HITES, 1978)) the alkyl homologs were found to be relatively abundant; at higher flame temperatures [combustion of petroleum fuels (LEE *et al.*, 1977)] lower relative amounts of alkylated PAH compounds were produced. The dominant fuel of the Providence–Narragansett Bay area is petroleum. Since the AHDs in air particulates have been found to reflect the fuel type of the area (HASE and HITES, 1976; LEE *et al.*, 1977), steeply negatively sloping AHDs (showing low relative abundance of alkylated PAH compounds) in air particulates of this area would have been expected. While no air samples were obtained in the present study, the 'corrected' (see Methods) $Z = -18$ and $Z = -22$ AHDs from the pond sample were steeply negatively sloping and closely resembled the uncorrected distributions shown (Figs 4 and 5). The AHDs of the pond sediments and the dominant fuel usage of the area combined to suggest that the AHDs of airborne particulates in the Providence–Narragansett Bay area would probably have been steeply negatively sloping, and would have resulted from the combustion of petroleum fuels.

The transect sediment sample AHDs, although more similar to those of the combustion inputs, show evidence of petroleum inputs for the sites closer to Providence. For these samples, the AHDs (especially the $Z = -18$) are much less steeply negatively sloped; i.e. they show higher relative concentrations of the alkyl homologs (Figs 4 and 5). These distributions can be closely matched by mathematically combining those of the two input materials in proper relative amounts. For example, for the $Z = -22$ AHD, a combination of 80% Jamestown Pond + 20% used motor oil gives the approximate distribution observed at Sabin Point. The reason for the higher proportion of petroleum PAHs in the upper bay stations was unclear, but these higher relative concentrations may have resulted from the differential settling of petroleum contaminated particles in the upper bay.

This study also determined that the P/As constitute another means of differentiating among samples. For instance, the P/As calculated from wood stove combustion products or from coal tar (produced by prolonged periods at high temperatures) were relatively high (Table 1). Data from another study showed a relatively high P/A for the combustion products of kerosene, but the exact ratio could not be determined because the phenanthrene gas chromatographic peak was off scale (LEE *et al.*, 1977). A P/A of 15 was found in airborne particulate material in Zurich, Switzerland (GIGER and SCHAFFNER, 1978). The P/A of the pond sediment from the present study was 18. The dominant fuel of the area (petroleum) and the P/A in the pond sediment combined to suggest that the P/A in the airborne particulates would have been relatively high. On the other hand, the No. 2 fuel oil P/A was very high (50), while the used motor oil P/A was quite low (8). The transect sediments, however, all had P/As which were very low (3.0–4.3). Thus, although the P/As can be used to differentiate among sample types, the proposed combination of combustion and petroleum inputs does not easily explain the uniformly low P/As found in transect sediments. For upper bay sediments a combination of inputs of used motor oil and combustion products would result in a lower P/A ratio than that from combustion products alone, but not as low as that found in the sediments. In addition, this combination of inputs does not easily explain the low P/As found in lower bay sediments where the input of oil is greatly reduced. Apparently some other process(es) must be working to lower this ratio. Since the solubility of phenanthrene is $\simeq 20$ times that of anthracene (MAY *et al.*, 1978), solubility fractionation could account for the lower ratios in the sediment samples. However, other differences (e.g. reactivity, or susceptibility to bacterial degradation) between these two isomers may have caused the observed decrease. In any case, any sizeable decrease in the absolute level of phenanthrene should also cause a slight relative decrease in the first point of the PCDs. In fact, comparisons of PCDs of input materials and sediments (Fig. 3) show that there may be such a slight decrease.

In the past, other researchers have hypothesized that the decreasing aqueous solubility of PAHs with increasing alkylation (MCAULIFFE, 1966; SUTTON and CALDER, 1974, 1975; MAY *et al.*, 1978) may have caused the alteration of AHDs in airborne particulates to those found in marine sediments (HASE and HITES, 1976; HITES, 1976; LAFLAMME and HITES, 1978). In this hypothesis the greater aqueous solubilities of the first members of a homolog series were believed to cause these molecules to be fractionated into the water; the lower water solubilities of the more highly alkylated PAH molecules were believed to result in them adhering to particulate material and eventually being deposited in marine sediments. This solubility fractionation resulted in less steeply negatively sloped AHDs in marine sediments. Two observations of the present study were not consistent with this hypothesis. The first is that the steeply negatively sloping AHDs of the pond sediment were not altered by this process. The second is that although past research has also shown that the solubility of the compounds used to calculate PCDs decreases rapidly

with increasing molecular weight (MAY *et al.*, 1978), the transect PCDs show no evidence of solubility fractionation; i.e. they are very similar to the pond PCD, which is representative of atmospheric input.

This study also determined that these combustion related PCD's are very similar to those of sediment samples obtained near and at some distance from Boston (calculated from the data of WINDSOR and HITES (1979). This close agreement of PCDs from a wide variety of samples is consistent with expectations from the combined inputs hypothesis. Petroleum contains only small amounts of parent PAH compounds relative to their alkylated homologs (Figs 4 and 5), and the concentrations of these parent compounds drop off quickly with increasing molecular weight (Fig. 3). In addition, for combustion inputs the parent compounds occur at much higher concentrations than their alkylated homologs. These three facts considered together indicate that the effect of an input of PAH from petroleum on a PCD representative of combustion products would be seen only in the early members of the distribution and would be dramatically lower in level than the effect of this input on the AHDs.

CONCLUSIONS

The present study found rapidly decreasing concentrations of PAH compounds with increased distance from Providence and found that the PAH assemblages in Narragansett Bay sediments showed evidence for at least three possible origins. The sediments surrounding tarred piers were contaminated by coal tar used to coat the pilings. Evidence for the input of PAHs from petroleum (presumably via sewage outfalls) to bay sediments appeared in the $Z = -18$ and, to a much lesser extent, in the $Z = -22$ AHDs of upper bay transect sediments. The influence of this input became less apparent in AHDs of samples from the lower (less polluted) end of the transect. The close resemblance of PCDs from bay sediments and combustion products indicated that the dominant origin of PAHs in the transect sediments probably resulted from combustion processes. The present study found that the PCDs and AHDs from transect sediments of Narragansett Bay could best be explained by a combination of inputs of PAHs from petroleum and combustion processes, rather than by the alteration of PAH assemblages of incoming airborne material by the solubility fractionation process. While a solubility fractionation may have changed the relatively high P/As found on airborne material to the low values found in transect sediments, other processes (related to reactivities or to selective bacterial degradations of these isomers) may have been responsible for the decreases in this ratio. While a combustion origin seemed likely for much of the PAH content of transect sediments, data from the present study were insufficient to determine whether these compounds entered the bay from urban runoff (including sewage discharge), or were deposited directly on bay water from the atmosphere. Due to the toxicity of PAH compounds and their utility as indicators of anthropogenic inputs to the environment, more information on the formation, transport, modification, and health hazards of these compounds is greatly needed.

Acknowledgements—The authors wish to thank Dr JOHN FARRINGTON and Dr JAMES QUINN for their careful reviews of the manuscript. The support of Grant No. R805477 from the Environmental Protection Agency is also greatly appreciated.

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